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CLAY/RUBBER NANOMETER COMPOSITE MATERIAL MANUFACTURING METHOD

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Abstract

The present invention pertains to a method for manufacturing a clay/rubber nanometer composite material. The method of the present invention is based on the fact that most rubber materials have their own emulsion forms. After an aqueous suspension of clay is mixed with a rubber emulsion, an agglutinant is added for flocculation, followed by dewatering to obtain a

clay/rubber nanometer composite material. The method of the present invention has simple operation, low cost, and a wide application range and is easy to industrialize. By using the method of the present invention, clay can be dispersed uniformly in nanometer order in the clay matrix.

### Claims

1. A clay/rubber composite nanometer composite material manufacturing method having the following steps: A: a suspension consisting of water and a clay with an overlapped crystal layer structure is mixed with a rubber emulsion to obtain a homogenous mixed solution; B: an agglutinant that can demulsify the rubber emulsion is added for flocculation; C: the obtained flocculate is dewatered and dried to obtain a clay/rubber nanometer composite material.

2. The manufacturing method described in Claim 1 characterized by the fact that the weight percentage of the clay in the suspension consisting of water and clay is in the range of 0.2-20%.

3. The manufacturing method described in Claim 1 characterized by the fact that the aforementioned agglutinant is an electrolyte solution.

4. The manufacturing method described in Claim 1 characterized by the fact that the aforementioned clay is Verona green, montmorillonite, saponite, beidellite, hectorite, silica, or halloysite.

5. The manufacturing method described in Claim 1 characterized by the fact that the aforementioned clay is a sodium-based bentonite.

6. The manufacturing method described in any of Claims 1-5 characterized by the fact that microwaves or ultrasonic waves are applied in step A.

7. The manufacturing method described in any of Claims 1-5 characterized by the fact that a substance that has a coupling effect between the clay and the rubber macromolecules is added in step A.

The present invention pertains to a method for manufacturing a polymer-based nanometer composite material, especially a rubber-based nanometer composite material. More specifically, the present invention pertains to a method for dispersing layers in nanometer size containing clay particles in rubber.

Carbon black and white carbon black have been used as conventional reinforcing agents in the rubber industry. Especially, the former is very important in the rubber industry. The original particles of these two reinforcing agents have a very small size. For example, the particle sizes of carbon blacks prior to the N600 grade are all smaller than 60 nm. The particle size of white carbon black produced using the precipitation method is usually in the range of 20-40 nm.

The particle size is the primary factor that affects the rubber reinforcing capability of a reinforcing agent. When the particle size exceeds 1000 nm, even if a surface processing method is used to create excellent interface bonding between two components, it is very difficult to reach the reinforcing level of carbon black or white carbon black. Study of a large number of inorganic fillers has proved this point. Up to now, it has not been possible to find a new filler with better reinforcing capability than the aforementioned two reinforcing agents because newly developed fillers all have relatively large particle sizes.

However, efforts to develop new rubber reinforcing methods and reinforcing agents have never stopped. This is because conventional reinforcing agents have the following disadvantages. (1) The processing pollution is severe. Since these two reinforcing agents have very low apparent density, they can easily blow around when added into rubber. Therefore, even if a sealed mixing machine is used, it is very difficult to keep a mixing workshop clean and avoid harm to a worker's health. (2) The processing time is long, and the mixing energy consumption is large. Since the powders of these two reinforcing agents are very fine, they readily aggregate. Therefore, a relatively long period of time is necessary to disperse them in rubber. In the meantime, because of the extremely low apparent density, a relatively long period of time is necessary to mix (or knead) the reinforcing agent into rubber. The time for this step is almost  $\frac{1}{2}$  the time of the entire rubber mixing process. (3) The color tone of the product is monotonous. This problem mainly occurs when reinforcing with carbon black. High-grade carbon black is usually used in the rubber industry because it has a better general reinforcing capability than white carbon black. However, it is impossible to change the black color tone of the product. (4) Some properties are still less than perfect. For example, neither of these two reinforcing agents is able to provide rubber products with high hardness, superior air permeation resistance, etc. (5) Because of its reliability on petroleum, resources for carbon black are gradually being reduced. It is impossible for white carbon black to completely replace carbon black, and its cost is relatively high. For example, if a silane coupling agent is used for surface processing (this is required in many cases), the cost will be even higher.

Consequently, the development tendency of new reinforcing agents is to provide good processibility as well as relatively good general reinforcing capability. The best choice is a light color filler with a low cost. Results of studies on clay polymer based nanometer composite material give hope of solving the aforementioned problems.

The study of clay/polymer based nanometer composite materials currently is a hot topic in the polymeric material study field. A series of excellent physical and mechanical properties for this type of material has been displayed and industrialization results have already been provided. For example, a clay/nylon 6 nanometer composite material produced by Ube Industries Ltd. of Japan has very high rigidity as well as a very high thermal deformation temperature and

tensile strength. A series of polymer-based clay nanometer composite materials has been produced in the lab. Examples include nylon 6, epoxy resin, polystyrene, etc. These nanometer composite materials are obtained by using suitable technology to uniformly disperse the unique layer structure contained in the clay particles in a polymeric matrix. Since the thickness of a clay layer is around 1 nm, the thickness of the dispersion phase (single clay layer or layer aggregation) can be kept at 100 nm or smaller in the final composite material. Therefore, this type of material is called a nanometer composite material. These nanometer composite materials not only have very good tensile properties and processability but also have excellent air permeation resistance because of the existence of the clay layer. A recent study showed that composite materials also have excellent flame retardancy. In summary, these studies provide very good ideas for developing new rubber reinforcing methods and reinforcing agents.

Most of the clay/polymer based nanometer composite materials are manufactured through in situ polymerization. The in situ polymerization method means that a continuous phase and a nanometer dispersion phase are simultaneously obtained during the process of a chemical reaction. For example, Fukushima, et al. has successfully manufactured a clay/nylon 6 composite material by embedding cations of 12-aminododecanoic acid between the crystal layers of clay to obtain an organic clay and then initiating polymerization of the permeated caprolactone monomer between the crystal layers. Patent Filing No. 96105362.3 by the Chinese Academy of Science also disclosed a primary in situ polymerization method used for manufacturing a type of polyamide/clay nanometer composite material. In many cases, however, it is difficult to find a monomer like caprolactone which can readily enter the space between clay layers to carry out in situ polymerization to form a nanometer composite material. Therefore, this type of manufacturing method has limited application. Also, this type of method has a high cost, and the process is complicated and unstable. Therefore, realization of industrialization is difficult.

Compared to clay/plastic based nanometer composite materials, there are very few studies on clay/rubber-based nanometer composite materials. US4889885 (reference 1) disclosed two methods for manufacturing clay/rubber nanometer composite materials. One of them is an in situ polymerization method. In this method, first, clay layers are modified using a vinyl-terminated quaternary ammonium salt. Then, the modified clay is dispersed in an N,N-dimethylformamide solvent, followed by addition of a large amount of isoprene monomer and a radical initiator in a corresponding proportion. Polymerization of isoprene is initiated between the clay layers to form polyisoprene rubber. Then, the solvent is removed to obtain a clay/isoprene rubber nanometer composite material. In the other method, liquid amine-terminated nitrile rubber with a relatively low molecular weight is dispersed in a mixed solvent consisting of water and dimethyl sulfoxide, followed by adding an acid to form an amine salt, which is then mixed with an aqueous suspension of clay. Finally, the water and solvent are

removed to form a clay/liquid nitrile rubber nanometer composite material. Chinese Patent Filing No. 94192043.7 (reference 2) disclosed a method for manufacturing a clay/liquid nitrile rubber nanometer composite material used for an airtight layer in tires and inner tubes. In this case, first, clay is dispersed homogeneously in water, followed by adding an acid so that the surface of the clay layer will adsorb hydrogen ions. Then, this is mixed with a toluene solution of liquid amine-terminated nitrile rubber. During the mixing process, the hydrogen ions on the layer react with the terminal amine groups of the nitrile rubber. As a result, the clay layer is dispersed in the liquid nitrile rubber, and a nanometer composite material can be obtained by removing the solvent.

Theoretically, when the dispersibility of a clay layer in rubber increases, the obtained material will have higher hardness, a lower elongation rate, higher strength, less elasticity, better flame retardancy, and better air permeation resistance. For most rubber products, there is no need for the clay layer to form a complete monolayer dispersion state even if the tensile performance of the obtained composite material is very good. If the clay layer is dispersed in rubber in the form of a certain aggregate (such as several layers or even more than ten layers), the aggregate size is in the range of several nanometer to tens of nanometers, which makes it possible to obtain a clay/rubber nanometer composite material with excellent comprehensive performance. When the two methods described in reference 1 are compared to the method described in reference 2, the clay manufactured using the former has higher dispersibility, but the elasticity of the obtained material is a little less than the material manufactured using the latter. Reference 2 overcomes this problem. In its clay/rubber nanometer composite material, the clay layer exists in the form of a certain degree of aggregate to not only satisfy the required air permeation resistance but also to offer a relatively good elasticity. From the point of view of method implementation, the in situ polymerization method described in reference 1 is too complicated and is thus very difficult to industrialize. The method described in reference 2 and the second method described in reference 1 are still relatively complicated even though the processing is slightly simplified. Also, the amine-terminated nitrile rubber needed is relatively expensive, and a large amount of relatively expensive solvent is needed during the manufacturing process. More importantly, the obtained nanometer composite material must be used by being mixed with other solid-state rubbers because of the low strength and high price of the liquid nitrile rubber. However, liquid nitrile rubber has very poor compatibility with many solid-state rubber materials (such as natural rubber, styrene-butadiene rubber, cis-1,4-polybutadiene rubber, ethylene-propylene rubber, etc.). As a result, the performance of the composite material obtained is adversely affected.

The objective of the present invention is to provide a new clay/rubber nanometer composite technology, which offers a simple operation, low cost, and wide application range and

is easy to industrialize. By using this method, clay can be homogeneously dispersed in nanometer order in a rubber matrix.

The method of the present invention is based on the fact that most rubber materials have their own emulsion forms. After an aqueous suspension of clay is mixed with a rubber emulsion, an agglutinant is added for flocculation, followed by dewatering to obtain a clay/rubber nanometer composite material.

The clay/rubber composite nanometer composite material manufacturing method disclosed in the present invention has the following steps: A: a suspension consisting of water and a clay with an overlapped crystal layer structure is mixed with a rubber emulsion to obtain a homogenous mixed solution; B: an agglutinant that can demulsify the rubber emulsion is added for flocculation; C: the obtained flocculate is dewatered and dried to obtain a clay/rubber nanometer composite material.

The clay used in the present invention can be a natural or synthetic clay, such as Verona green, montmorillonite, saponite, beidellite, hectorite, silica, or halloysite. It is preferable to use a clay with sodium ions as interlayer cations, such as a sodium-based bentonite, in the present invention. The clay used should have an overlapped crystal layer structure so that it can be separated and dispersed in nanometer size in the rubber. The adjacent crystal layers in this type of clay have negative electric charges. Therefore, cations are usually adsorbed between the crystal layers of the clay. This type of structure allows water or other polar molecules to enter the space between the crystal layers of the clay so that the external cations can interchange with internal anions. When the clay is mixed with water, a stable aqueous suspension of clay is formed. In the suspension, the crystal layers of the clay are separated from each other under the hydration effect of the interlayer cations. When the rubber emulsion is added, the crystal layers of the clay are interwoven with the emulsion particles to be separated from each other. If an agglutinant that can demulsify the rubber emulsion is added at that time for flocculation, the nanometer composite structure of the two components is retained to form a clay/rubber nanometer composite material.

The dispersion distance of the clay layers in water depends on the concentration. The concentration cannot be too high. The higher the concentration is, the smaller the dispersion distance. As a result, it is difficult for the emulsion particles to interweave with the clay layers, and the size of the nanometer dispersion phase is increased. If the concentration is too low, coagulation of the final clay/emulsion mixture occurs with difficulty. Therefore, the content of the clay in the suspension consisting of water and clay should be kept in the range of 0.2-20% (by weight).

After the clay is mixed with water, the system can be allowed to stand still for a certain period of time to allow precipitation of some clay particles, which have a relatively large specific

weight and are very hard to disperse, as well as sand contained in the clay. Aqueous suspension of clay prepared in this way is finer. However, whether to allow the system to stand still and the period of standing time can be determined depending on the quality and properties of the clay.

The present invention has no special requirement for the agglutinant used. Different agglutinants can be used depending on the type of emulsion used. An agglutinant necessary to industrially agglutinate a corresponding type of emulsion can be used. For example, a hydrogen chloride solution with a concentration of about 1.5% (by weight) can be used for a styrene-butadiene emulsion, and a calcium chloride solution with a concentration of about 2% (by weight) can be used for a nitrile rubber emulsion.

The method of the present invention has no special requirement for the rubber emulsion, which can be either an emulsion obtained prior to the agglutination step during a rubber synthesis process or a re-emulsified product of a rubber. There is no special limitation on the type of emulsion or the solids content of the emulsion. Examples of emulsions that can be used include a styrene-butadiene rubber emulsion, nitrile rubber emulsion, chloroprene rubber emulsion, acrylic rubber, etc. It is also possible to use a mixture of two or more types of emulsions to obtain nanometer composite materials with mixed matrix materials having a wide application range. Some plastic matrixes having an emulsion form can also be used in the method of the present invention to manufacture clay/plastic based nanometer composite materials. Examples of such emulsions include a polyvinyl chloride emulsion, polystyrene emulsion, etc.

In the method of the present invention, it is also possible to apply microwaves or ultrasonic waves in step A so that the clay layers will be better dispersed in the rubber matrix.

In the method of the present invention, it is also possible to add a substance with a coupling effect in step A to increase the interface effect between the clay layer and the rubber matrix. Examples of coupling agents that can be used include commercially available triethanolamine, a silane coupling agent, a coupling agent of an organic titanate, etc. The amount of the coupling agent added is in the range of 0.2-5% (by weight) of the amount of clay used.

The clay/rubber nanometer composite material manufacturing method disclosed in the present invention has a simple operation and a low cost. There is no pollution in the manufacturing process. For a clay/rubber nanometer composite material manufactured using the method of the present invention, the dispersion phase is an aggregate of clay monolayers or layers with a thickness of 100 nm or smaller. It has excellent physical and mechanical properties, processibility, and fairly good air permeation resistance. It can replace expensive butyl rubber or butyl chloride rubber used for the inner tubes of tires or for airtight layer adhesives of tires having no inner tubes. The clay/rubber nanometer composite material manufactured using the

method of the present invention can be directly added into a sulfide system, softened body system, etc. It can also be used together with other types of raw rubber materials or reinforcing agents (such as carbon black, white carbon black, calcium carbonate, pottery clay, etc.).

Also, since the clay layers have already been dispersed homogeneously as a reinforcing agent in the rubber matrix in advance, there is no need to add carbon black, or only a small amount of carbon black has to be added. This will significantly reduce the environmental pollution caused by flying dust generated during the rubber mixing process. In the meantime, it will also reduce the mixing time and lower the mixing energy requirement. In particular, this type of rubber material also has good compatibility with other additives. Compared to the methods described in references 1 and 2, the method of the present invention has a simple process and no solvent pollution and does not need expensive liquid nitrile rubber as the "matrix" of the composite material for further dispersion in a normal rubber matrix.

**Application Example 1:** Commercially available bentonite was stirred in water for 4 h. After homogeneous mixing, the system was allowed to stand still for 24 h. The final concentration (solids content) was kept around 2% (by weight). 200 g of the suspension prepared as described above were mixed with 250 g of a nitrile rubber emulsion (weight content of acrylonitrile: 26%, solids content: 40%) at room temperature. Then, a 2% hydrochloric acid solution was used for flocculation. The flocculate was washed to a neutral pH and was then dried in an oven at 80°C for about 10 h. As a result, a clay/nitrile rubber nanometer composite material with a clay content of about 4 g clay/100 g nitrile rubber was obtained. Under observation using a transmission electron microscope, it was found that more than 80% of the clay layers were thinner than 30 nm. After this composite material was mixed and vulcanized, the tensile strength was 15.0 MPa, and the elongation rate at break was 520%. On the other hand, the tensile strength of nitrile rubber doped with 10 parts by weight of high abrasion carbon black (N330) was only 6.0 MPa, and the elongation rate was 480%.

**Application Example 2:** A styrene-butadiene rubber emulsion was used instead of the nitrile emulsion used in Application Example 1. 400 g of a clay suspension with a solids content of 5% were mixed with 500 g of the styrene-butadiene rubber emulsion (solids content: 20%). Then, a hydrogen chloride solution with a concentration of around 2% was used for agglutination. The rest of the process was the same as that described in Application Example 1. A nanometer composite material with a clay content of 20 g clay/100 g styrene-butadiene rubber was obtained. After this composite material was mixed and vulcanized, the tensile strength was 12.0 MPa, and the elongation rate at break was 400%. On the other hand, the tensile strength of styrene-butadiene rubber doped with 20 parts by weight of high abrasion carbon black (N330) was only 10.0 MPa, and the elongation rate was 420%.

Application Example 3: When the aqueous suspension of clay was mixed with the styrene-butadiene rubber emulsion in Application Example 2, 0.8 g of a silane coupling agent KH560 (epoxy silane coupling agent produced by Nanjing Shuguang Chemical Factory) was added. The rest of the process was the same as that described in Application Example 2. After the obtained composite material was mixed and vulcanized, the tensile strength was 14.8 MPa, and the elongation rate at break was 300%. When no coupling agent was added, the tensile strength was 12.0 MPa, and the elongation rate at break was 400%. The tensile strength of styrene-butadiene rubber doped with 20 parts by weight of high abrasion carbon black (N330) was only 10.0 MPa, and the elongation rate was 420%.

Application Example 4: 200 g of a clay suspension with a solids content of 10% were mixed with 250 g of a nitrile rubber emulsion (solids content: 40%). The rest of the process was the same as that described in Application Example 1. A nanometer composite material with a clay content of 20 g clay/100 g nitrile rubber was obtained. After the obtained composite material was mixed and vulcanized, the tensile strength was 19.5 MPa, and the elongation rate at break was 570%. On the other hand, the tensile strength of nitrile rubber doped with 20 parts by weight of high abrasion carbon black (N330) was only 11.0 MPa, and the elongation rate was 500%. The air permeation resistance of the obtained material was 2.2 times that of the carbon black-doped material. The airtightness was improved by 30% compared to the butyl chloride rubber used as an airtight rubber layer for radial tires provided by the Beijing Tire Factory.

Application Example 5: 250 g of a clay suspension with a solids content of 5% were mixed with 500 g of a styrene-butadiene rubber emulsion (solids content: 20%). The rest of the process was the same as that described in Application Example 2. A nanometer composite material with a clay content of 40 g clay/100 g styrene-butadiene rubber was obtained. After the obtained composite material was mixed and vulcanized, the tensile strength was 17.0 MPa, and the elongation rate at break was 380%. On the other hand, the tensile strength of styrene-butadiene rubber doped with 40 parts by weight of N550 carbon black was only 13.0 MPa, and the elongation rate was 410%. The air permeation resistance of the obtained material was 1.7 times that of the carbon black doped material. The airtightness was improved by 40% compared to a natural rubber material for inner tubes of radial tires provided by the Beijing Tire Factory.

Application Example 6: In Application Example 1, ultrasonic waves were applied to the mixture of the clay suspension and the rubber emulsion for 10 min (using ultrasonic cleaning device CX-250 produced by the Second Beijing Medical Equipment Factory). The rest of the process was the same as that described in Application Example 1. After the obtained composite material was mixed and vulcanized, the tensile strength was 17.0 MPa, and the elongation rate at break was 490%. When ultrasonic waves were not applied, the tensile strength was 15.0 MPa,

and the elongation rate at break was 520%. The tensile strength of nitrile rubber doped with 10 parts by weight of high abrasion carbon black (N330) was only 6.0 MPa, and the elongation rate was 480%.

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[54]发明名称 粘土/橡胶纳米复合材料的制备方法

[57]摘要

本发明为一种粘土/橡胶纳米复合材料的制备方法。本发明的方法基于大多数橡胶均有自己的乳液形式的优势,利用粘土的水悬浮液与橡胶乳液进行共混,加入凝聚剂进行絮凝,脱去水份,从而获得粘土/橡胶纳米复合材料。本发明的方法操作简单、成本低、适用面广、易于工业化,使用本发明的方法可使粘土在橡胶基质中能够以纳米级的形式均匀地分散。

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## 权 利 要 求 书

1. 一种粘土/橡胶纳米复合材料的制备方法,依次包括如下步骤, A: 将具有层状晶层重叠结构的粘土和水的悬浮液与橡胶乳液混合,形成均匀的混合液; B: 加入可使橡胶乳液破乳的凝聚剂进行絮凝; C: 将絮凝物脱水、烘干制得粘土/橡胶纳米复合材料。

2. 根据权利要求1所述的制备方法,其特征是:所说的粘土和水的悬浮液中粘土的重量百分含量为0.2-20%。

3. 根据权利要求1所述的制备方法,其特征是:所说的凝聚剂为电解质溶液。

4. 根据权利要求1所述的制备方法,其特征是:所说的粘土为绿土、蒙脱土、滑石粉、贝得石、水辉石、硅石或多水高岭土。

5. 根据权利要求1所述的制备方法,其特征是:所说的粘土为钠基膨润土。

6. 根据权利要求1-5所述的任何一种制备方法,其特征是:在步骤A中,施加微波或超声波。

7. 根据权利要求1-5所述的任何一种制备方法,其特征是:在步骤A中加入具有能使粘土与橡胶大分子间产生偶联作用的物质。

## 粘土/橡胶纳米复合材料的制备方法

本发明涉及聚合物基纳米复合材料的制备方法，特别是橡胶基纳米复合材料的制备方法。更具体地，本发明涉及了一种将粘土颗粒中含有的纳米尺寸的片层分散在橡胶中的方法。

橡胶工业传统的补强剂一直是炭黑和白炭黑，特别是前者，在橡胶工业中占有重要地位。这两种补强剂原生粒子的尺寸是非常小的，如 N600 级别以前的炭黑，其粒径均小于 60 nm，沉淀法白炭黑的粒径一般也在 20-40nm 之间。可以说，粒子尺寸的大小是影响其对橡胶补强能力高低的第一因素，粒子尺寸超过 1000nm 后，即使用表面处理的方法使二者产生了优秀的界面粘合，也很难再达到炭黑和白炭黑补强的水平。对大量无机填料的研究，有力地证明了这一点，时至今日，也未能找到一种补强能力超过这两种补强剂的新型填料，原因是新发展的填充剂的粒径都较大。

然而，人们从未中断过对橡胶新型补强方式和补强剂开发的努力。这是因为，传统的补强剂具有以下缺点：（1）加工污染性大。由于这两种补强剂很低的视密度，因而在向橡胶中填加时，极易产生飞扬，因而即使使用密闭式炼胶机，也很难保证混炼车间的清洁，避免对工人健康的损害。（2）加工时间长，混炼能耗大。由于这两种补强剂的粉体极其细小，很容易聚集，因而在橡胶中分散所需要的时间较长，同时极低的视密度导致其向橡胶中混入（或称吃入）的时间也较长，几乎占橡胶混炼全过程的 1/2。（3）制品色调单一。这主要是指炭黑补强。高级别的炭黑一般较白炭黑有更好的综合补强能力，因而更常用于橡胶工业。但制品的黑色调却无法更改。（4）一些性能仍有欠缺。如这两种补强剂均很难赋予橡胶制品更高的硬度，更好的耐气透性能等等。（5）由于对石油的依赖性，因而炭黑的资源逐渐在减少。白炭黑不可能完全代替炭黑，且价格较贵，如使用硅烷偶联剂进行表面处理后（许多时候要求这样），价格就更高。

因此，新型补强剂的发展趋势是，要具有良好的加工性能，要有较好的综合补强能力，最好是浅色填料，价格要低。有关粘土聚合物基纳米复合材料的研究成果使人们在这一问题的解决上看到了曙光。

粘土/聚合物基纳米复合材料的研究，是当今高分子材料领域研究

## 说 明 书

的热点,它已经向人们展示了这类材料所具有的一系列优异的物理机械性能,并已有工业化的成果,如日本宇部兴产公司生产的粘土/尼龙6 纳米复合材料,具有极高的刚度、很高的热变形温度和拉伸强度。人们已经在实验室制备了一系列聚合物基体的粘土纳米复合材料,包括尼龙6、环氧树脂、聚苯乙烯等等。这些纳米复合材料的获取,是使用适当的技术方式,将粘土颗粒结构中所含有的独特的片层结构,均匀地分散在聚合物基体中得到的。由于粘土片层的厚度在 1nm 左右,因而最终的复合材料中,分散相(粘土片层单层或片层聚集体)的厚度尺寸均能保持在 100nm 以下,所以称这种材料为纳米复合材料。这些纳米复合材料不但具有很好的强伸性能和加工性能,而且由于粘土片层的存在,复合材料还兼具有优异的抗气透性能,最近的研究表明,复合材料的阻燃性能也非常出色。总之,这些研究为人们寻找新型橡胶补强方式和补强剂提供了一种很好的思路。

绝大多数粘土/聚合物基纳米复合材料是通过原位聚合的方法制备的。原位聚合的方法是指,在化学反应的过程中同时获得连续相和纳米级分散相。例如, Fukushima 等利用 12-氨基十二酸的阳离子嵌入粘土晶层之间,得到有机粘土,然后在晶层之间引发渗透的单体己内酰胺聚合,成功地制得了粘土/尼龙6 纳米复合材料。中国科学院化学所申请的 96105362.3 专利,也揭示了一种聚酰胺/粘土纳米复合材料的一次法原位聚合制备方法。但是,在许多情况下,并不总能找到如己内酰胺那样容易进入粘土层间进行原位聚合的单体,形成纳米复合材料。因此这种制备方法在适用面上有一定的局限,而且这种方法成本高,工艺复杂不稳定,难于实现工业化生产。

同粘土/塑料基纳米复合材料相比,粘土/橡胶基纳米复合材料的研究还很少。US4889885 (文献 1)公开了两种制备粘土/橡胶纳米复合材料的方法。其一是原位聚合法,即首先用端乙烯基的季铵盐对粘土片层的性质进行改性,然后将这种改性粘土分散在 N,N-二甲基甲酰胺溶剂中,加入大量的异戊二烯单体和相应比例的自由基类型的引发剂。异戊二烯便在粘土片层间引发聚合成为聚异戊二烯橡胶,脱去溶剂,这样便得到了粘土/异戊二烯橡胶纳米复合材料。其二是,将分子量较低的液体端胺基丁腈橡胶分散在由水和二甲基氧硫组成的混合溶剂中,然后加酸使其形成胺盐,再与粘土的水悬浮液进行混合,最后脱去水和溶剂,便形成了粘土/液体丁腈橡胶纳米复合材料。中国专利申请 94192043.7 号(文献 2)公开了一种制备用于轮胎气密层和

内胎的粘土/液体丁腈橡胶纳米复合材料的方法。具体是，首先将粘土均匀地分散在水中，加酸使其片层表面吸附氢离子，然后与液体端胺基丁腈橡胶的甲苯溶液进行混合，在混合过程中，片层上的氢离子与丁腈橡胶的端胺基发生反应，这样粘土片层便分散在液体丁腈橡胶中，脱去溶剂便形成纳米复合材料。

理论上讲，粘土片层在橡胶中的分散性越高，所得材料的硬度就越高，伸长率越低，强度越高，弹性越差，阻燃性越好，抗气透性越优良。因此，对大多数橡胶制品而言，粘土片层也没有必要形成完全的单层分散状态，尽管得到的复合材料的强伸性能非常优良。若粘土片层以一定的聚集体（如几层甚至十几层）分散在橡胶中，其尺寸为几个纳米-几十纳米，可获得综合性能非常好的粘土/橡胶纳米复合材料。文献1的两种方法与文献2的方法相比，前者粘土有着更高的分散度，但所得到的材料弹性要差些。文献2克服了这一点，在所获得的粘土橡胶纳米复合材料中，粘土片层是以一定程度的聚集体存在的，既满足了所需要的抗气透性，弹性也较好。从方法的实施上讲，文献1提到的原位聚合方法过于复杂，很难实现工业化。文献2和文献1的第二种方法虽然工艺略有简化，但仍较复杂，而且所需要的端胺基丁腈橡胶价格较贵，工艺过程需要大量的价格较贵的溶剂。更重要的是所获得的纳米复合材料由于液体丁腈橡胶的强度和价格问题，而必须要与其它固态橡胶进行共混使用，而液体丁腈橡胶与许多固态橡胶（如天然橡胶、丁苯橡胶、顺丁橡胶、乙丙橡胶等）的相容性很差，从而使最终的复合材料性能受损。

本发明的目的是提出一种操作简单、成本低、适用面广、易于工业化的新型粘土/橡胶纳米复合技术，使得粘土在橡胶基质中能够以纳米级的形式均匀地分散。

本发明的方法基于大多数橡胶均有自己的乳液形式的优势，利用粘土的水悬浮液与橡胶乳液进行共混，加入凝聚剂进行絮凝，脱去水份，从而获得粘土/橡胶纳米复合材料。

本发明的粘土/橡胶纳米复合材料的制备方法，依次包括如下步骤，A：将具有层状晶层重叠结构的粘土和水的悬浮液与橡胶乳液混合，形成均匀的混合液；B：加入可使橡胶乳液破乳的凝聚剂进行絮凝；C：将絮凝物脱水、烘干制得粘土/橡胶纳米复合材料。

本发明所用的粘土可以是天然的或合成的粘土，包括绿土、蒙脱土、滑石粉、贝得石、水辉石、硅石及多水高岭土，其中本发明优选

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的是层间阳离子为钠离子的粘土，如钠基膨润土。所用的粘土需具有层状晶层重叠结构，以便能够以纳米尺寸分离并分散在橡胶中。这类粘土相邻晶层带有负电荷，因此，粘土晶层间一般吸附着阳离子，这种结构使得水和其它极性分子能进入粘土晶层之间，并可发生外界阳离子与内部阳离子间的交换作用。将粘土与水搅拌混合，便会形成一个稳定的粘土水悬浮体，其中的粘土晶层在层间阳离子的水化作用下，彼此分离。将橡胶乳液混入，粘土晶层便会与乳胶粒彼此间穿插而相互隔离。此时加入可使橡胶乳液破乳的凝聚剂进行絮凝，二者的微观纳米复合结构便会保留下来，从而形成粘土/橡胶纳米复合材料。

粘土片层在水中的分散间距取决于其浓度，浓度不能过大，浓度越高，分散间距越小，乳胶粒越难对其进行穿插隔离，纳米分散相的尺寸就会增大。而浓度过低，会使最终的粘土/乳液混合液的共凝聚发生困难。因此，粘土与水的悬浮液的含量宜控制在 0.2-20%（重量）

粘土与水混合后，经搅拌后可适当地静置一段时间，使比重较大的某些极难分散的粘土颗粒和含带的砂砾沉降下来，这样所得到的粘土水悬浮液更细腻。但静置与否和静置时间长短可根据粘土的品质和性质来决定。

本发明对所用的凝聚剂没有特别要求，但根据所使用的胶乳类型的不同可有所不同，使用相应类型的胶乳在工业化凝聚时所需要的凝聚剂便可。如丁苯橡胶乳液可使用 1.5% 左右（重量）的氯化氢溶液，丁腈橡胶乳液可使用 2% 左右（重量）的氯化钙溶液。

本发明的方法对橡胶乳液没有特别要求，可以是橡胶合成工艺过程中凝聚之前的乳液，也可以是橡胶再乳化产品，品种不限，胶乳固含量不限。如：丁苯橡胶乳液、丁腈橡胶乳液、氯丁橡胶乳液、丙烯酸酯橡胶乳液等等。也可以使用两种或两种以上的乳液的混合液，得到使用范围更为广泛的混合基体材料的纳米复合材料。一些具有乳液形式的塑料基体也可用本发明的方法制得粘土/塑料基纳米复合材料。如：聚氯乙烯乳液、聚苯乙烯乳液等等。

本发明的方法还可以在步骤 A 中施加微波或超声波，会使粘土片层在橡胶基质中得到更好的分散。

本发明的方法还可以在步骤 A 中加入具有偶联作用的物质，以增强粘土片层与橡胶基体间的界面作用。如市售的三乙醇胺、硅烷偶联剂；钛酸酯偶联剂等，用量为粘土用量的 0.2-5%（重量）。

本发明的制备粘土/橡胶纳米复合材料的方法，工艺简单、成本

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低、生产过程无污染。利用本发明的方法制得的粘土/橡胶纳米复合材料，其分散相为粘土单片层或片层的聚集体，厚度在 100nm 以下。具有优异的物理机械性能，加工性能。而且还具有相当好的抗气透性能，可代替价格昂贵的丁基橡胶或氯化丁基橡胶用在轮胎的内胎或无内胎轮胎的气密层胶上。利用本发明的方法制得的粘土/橡胶纳米复合材料，既可以直接加入硫化体系、软化体系等加以应用，也可以再加入其他类型的生胶或补强剂（如：炭黑、白炭黑、碳酸钙、陶土等）来加以应用。

另外，由于粘土片层作为增强剂已事先均匀地分散于橡胶基质中，因而可以不加入炭黑或少量加入炭黑，这将大大减少橡胶混炼过程中由于粉尘飞扬而造成的环境污染，同时减少混炼时间，降低混炼能耗。特别是这种胶料对其他配合剂的吃人性也很好。本发明的方法与文献 1 和文献 2 的方法相比，工艺简单，既无溶剂污染，也不需价格昂贵的液体丁腈橡胶作为复合材料的“基质”进而再向通用橡胶基质中分散。

实施例 1：将市售钠基膨润土在水中进行搅拌，时间为 4 小时，混合均匀后静置 24 小时，最终浓度（固含量）控制在 2%（重量）左右；将上述悬浮液 200 克与 250 克丁腈橡胶胶乳（丙烯腈重量含量为 26%，固含量为 40%）进行搅拌混合，温度在室温即可；然后用 2% 的盐酸溶液进行絮凝。对絮凝物进行冲洗，至中性。在 80℃ 烘箱中烘干，约 10 小时，得到粘土含量约为 4 克粘土/100 克丁腈橡胶的粘土/丁腈橡胶纳米复合材料。在透射电子显微镜下进行观察，粘土片层的厚度尺寸 80% 以上在 30nm 以下。以此复合材料进行混炼加工，硫化后，拉伸强度为 15.0MPa，扯断伸长率为 520%。而加入 10 重量份高耐磨炭黑（N330）的丁腈橡胶，其拉伸强度则只有 6.0MPa，扯断伸长率为 480%。

实施例 2：将实施例 1 中的丁腈胶乳改为丁苯橡胶胶乳，将固含量为 5% 的粘土悬浮液 400 克与 500 克丁苯橡胶胶乳（固含量为 20%）进行搅拌混合，用 2% 左右的氯化氢溶液进行凝聚。其它步骤同实施例 1。得到粘土含量为 20 克粘土/100 克丁苯橡胶的纳米复合材料。经混炼加工，硫化后，拉伸强度为 12.0MPa，扯断伸长率为 400%。而加入 20 重量份高耐磨炭黑（N330）的丁苯橡胶，其拉伸强度则只有 10.0MPa，扯断伸长率为 420%。

实施例 3：在实施例 2 中，在粘土水悬浮液与丁苯橡胶乳液混合

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时,加入 0.8 克的硅烷偶联剂 KH560 (环氧基硅烷偶联剂,南京曙光化工厂生产),其它步骤同实施例 2。将得到的复合材料进行混炼加工,硫化后,拉伸强度为 14.8MPa,扯断伸长率为 300%,不加偶联剂的拉伸强度为 12.0MPa,扯断伸长率为 400%。而加入 20 重量份高耐磨炭黑 (N330) 的丁苯橡胶,其拉伸强度则只有 10.0MPa,扯断伸长率为 420%。

实施例 4: 将固含量为 10%的粘土悬浮液 200 克与 250 克丁腈橡胶胶乳 (固含量为 40%) 进行搅拌混合,其它步骤同实施例 1。得到粘土含量在 20 克粘土/100 克丁腈橡胶的纳米复合材料,经混炼加工,硫化后,拉伸强度为 19.5MPa,扯断伸长率为 570%。而加入 20 重量份高耐磨炭黑 (N330) 的丁腈橡胶,其拉伸强度则只有 11.0MPa,扯断伸长率为 500%。所得材料的抗透气性能是炭黑胶料的 2.2 倍,比北京轮胎厂提供的子午线轮胎用氯化丁基橡胶气密层橡胶的气密性提高了 30%。

实施例 5: 将固含量为 5%的粘土悬浮液 250 克与 500 克丁苯橡胶胶乳 (固含量为 20%) 进行搅拌混合,其它步骤同实施例 2。得到粘土含量为 40 克粘土/100 克丁苯橡胶的纳米复合材料。经混炼加工,硫化后,拉伸强度为 17.0MPa,扯断伸长率为 380%。而加入 40 重量份 N550 炭黑的丁苯橡胶,其拉伸强度则只有 13.0MPa,扯断伸长率为 410%。所得材料的抗透气性能是炭黑胶料的 1.7 倍,比北京轮胎厂提供的子午线轮胎用天然橡胶内胎胶料的气密性提高了 40%。

实施例 6: 在实施例 1 中,将粘土悬浮液与橡胶乳液的混合液加载超声波 10 分钟 (采用北京医疗设备二厂生产的 CX-250 超声清洗器),其它步骤同实施例 1。对所得材料进行混炼加工,硫化后,拉伸强度为 17.0MPa,扯断伸长率为 490%,而不加超声波的拉伸强度为 15.0MPa,扯断伸长率为 520%。而加入 10 重量份高耐磨炭黑 (N330) 的丁腈橡胶,其拉伸强度则只有 6.0MPa,扯断伸长率为 480%。

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